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<p>Much effort has been expended in trying to understand and predict the unusual phenomena which can occur when initially glassy polymers are exposed to small-molecule gases, organic vapors or liquids. Sorption of the gas or vapor seems to occur at two distinctly different sorption sites (dual mode sorption), and influx of the penetrant leads to a non-Fickian front traveling at constant velocity (case-II diffusion). Because traditional measurement techniques such as sorption and permeation are complicated by these very phenomena which they try to explain, attempts to determine to what extent these phenomena are governed by diffusive characteristics of glassy transport rather than by the interplay of diffusion and polymer relaxation have been frustrated. Instead, a method of observing diffusion which does not require penetrant transport across a surface and influx into the sample must be used.</p> <p>(continued on reverse)</p>				
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We have used the Holographic Relaxation Spectroscopy (HRS) technique to eliminate the stumbling blocks mentioned above. HRS allows us to observe the self-diffusion of a probe dye molecule dispersed homogeneously in a polymer or polymer-diluent mixture at equilibrium, thus eliminating complications mentioned above. The diffusion is measured on length scales in the micron range, by creating a spatially periodic variation in dye concentration with a flash of laser light; the rate of disappearance of this pattern is proportional to the diffusion coefficient. Using HRS, we can measure self-diffusion coefficients (D_{self}) ranging from 10^{-5} to 10^{-16} cm²/sec. This allows measurement in systems ranging from pure diluent to glassy bulk polymer. With the capabilities of HRS at our disposal, we are addressing the following questions concerning the nature of small molecule transport in glassy and non-glassy systems:

- 1) What is the effect of diffusant molecular size on its transport?
- 2) What is the effect of the glass transition on $D_{\text{self}}(c, T)$?
- 3) Does free volume theory, which has been very successful for predicting solvent and probe diffusion in non-glassy systems by relating the mobility of small molecules to the existence of void space, or "free volume", in solution, work as well for diffusion of probes below T_g ?

In order to answer these questions, we have measured D_{self} of two photochromic probes in polystyrene-toluene solutions over a wide range of temperature, above and below the glass transition. We have analyzed these data according to free volume theory for small molecule diffusion in non-glassy and glassy systems.

We have found, as expected, that the size of the diffusing molecule has a strong effect on its diffusion coefficient, and also that the diffusion coefficient of the probe in a polystyrene-toluene solution can be correlated to the toluene self-diffusion coefficient.

The effect of the glass transition on D_{self} has been measured. We have diffusion data from three PS toluene solutions, 81%, 83%, and 84% PS, versus temperature. There is clearly an abrupt change in the temperature dependence of D_{self} near T_g for each solution, with the abruptness of the change increasing with polymer concentration.

The predictions of the Vrentas-Duda free volume theory for glassy solutions have been examined. Although the theory is qualitatively correct in predicting the change in $D_{\text{self}}(T)$ at T_g and the effect of increasing polymer concentration on that change, the figure clearly shows that it does not agree quantitatively with the diffusion data. This is due to an inherently unrealistic representation of the polymer contribution to the glassy solution free volume. Thus, while the Vrentas-Duda theory is able to rationalize the diffusion data which we obtained, it is insufficient for a quantitative prediction of glassy self diffusion.

The substance of the work is described in two accompanying research reports.



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